23 MAR 1977

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⑫ 5 p.

⑪ 9 February 1977

by

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⑭ X77-152/101

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OCT 18 1978

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Presented to

International Microelectronics Conference/WEST
Anaheim, Ca.
1-3 March 1977
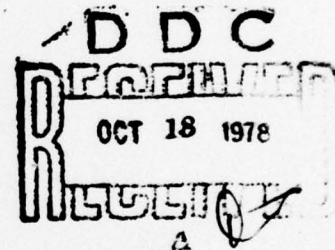
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AQUEOUS DEPOSITION OF PROTECTIVE SYSTEMS FOR ELECTRONIC STRUCTURES

by

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Electronic Structures - Definition

Electronic structures are those electromechanical parts which are used to enclose devices and modules, to attach them to subsystems, or to interconnect them electrically. Included in this category of parts are boxes, support frames, fasteners, springs, connectors, contacts and lead wires.

Functions of the Structures

The prime function of electronic structures is to provide mechanical support and protection. However, additional functions are often required for military hardware. The first of these is to maintain electrical continuity in order to shield the electronics from EMI and radiation effects. Another is to protect the system from heat from rocket engines or nuclear explosions.

Materials

Material choice is dictated by physical and chemical properties requirements and by economics. The latter is always a heavily weighting factor.

In aerospace applications, the structural material must be the lightest that is capable of providing the desired properties. Any weight reduction effects economic saving in fuel, the amount varying with, for example, the distance requirement per unit fuel consumption.

Thus, the light metals, aluminum and magnesium, are the appropriate choices for boxes. However, their greater chemical activity increases the difficulty of inhibition of corrosion, both atmospheric and galvanic. This latter is induced by contact of the light metal (anodic) with heavier metals (cathodic), which might be fasteners. Such galvanic action could occur also at discontinuities in plated metals, which are also cathodic.

Consequently, special corrosion inhibiting techniques have been and are currently being developed to improve the usefulness of the light metals during the time periods and within the range of environments in which the electronics are required to function.

Exemplifying are protective finishes for aluminum, e.g., chromates. The combination of corrosion resistance, paint base, low electrical resistance and low price is best achieved with chromate films. MIL-C-5541, Chemical Films for Aluminum, Class 3, requires that alloys with such films shall be un-corroded by 168 hours exposure to 5% salt fog test and that the electrical resistance of the film shall be no greater than 5 milliohms when measured under 200 pound force applied over a one square inch circular area. This thin film is the most powerful of the aluminum finishes. Although its thickness varies with the amount of absorbed water, thickness is not a real consideration. The film can be crushed or abraded without reduction of its protective value. When it is scratched, it heals itself by reaction of atmospheric moisture dissolving the soluble constituents of the film, which reacts with the freshly exposed aluminum to restore the film.

Although process control is critical, the chromating process is simple in that minimal equipment and process time is required.

First, the aluminum must be made chemically clean, i.e., free of soils and oils. Next the oxide is dissolved. Although the oxide is immediately reformed, the thin, freshly-formed oxide is free of contaminants and more readily activated than the one removed.

The chromating process consists of reaction of the relatively active aluminum surface with an acid solution containing hexavalent chromium and accelerators. Remarkably, the chromating solution is dilute and, hence, inexpensive. The reaction time is in the range of one to three minutes.

More remarkably, in an experiment, during which sliding wear penetrated not only the film, but the aluminum to a depth of three or four thousandths of an inch and width in excess of one-fourth inch, salt spray tests demonstrated that the film healed itself and inhibited corrosion.

Processes have been so developed as to reliably produce films which, while inhibiting corrosion, are low enough in electrical resistance to comply with the requirements of MIL-B-5087 "Electrical Bonding." This specification, which constitutes the electromagnetic bonding requirement of modern aerospace contracts, stipulates that at each bond, the maximum electrical resistance shall be 2.5 milliohm.

Anodic Films

These films are formed, as suggested by the name, by making the aluminum anodic in an electrolyte, most commonly chromic or sulfuric acid. The aluminum is prepared for anodizing in the same way that it is prepared for chromating. Next, it is electrolyzed at a current which has been experimentally proven to produce an optimum oxide film. After rinsing, a critical sealing operation is performed. It consists of soaking the oxidized aluminum in water at a temperature near boiling and containing corrosion inhibitors such as hexavalent chromium. Finally, it is rinsed in cold water and dried. The resultant film immediately adjacent to the aluminum is a monohydrate of the oxide.

Obviously, during the sealing operation, the aluminum expands opening the oxide film to allow exchange of entrapped oxidizing electrolyte with the sealing solution. In the subsequent cold rinse, the aluminum contracts, causing the oxide film to contract, consequently entrapping the corrosion inhibiting sealing solution.

For many years and currently, anodic films, alone and coated with organic paints, have been the preferred protective finishes for aluminum in military and aerospace applications. However, modern research (Reference a) has proven that, in protecting high strength alloys from stress corrosion, the anodic films were inferior to chromates. Since the anodizing process requires so much more material and equipment, i.e., electrical power sources, wiring, contact materials, etc., it is much more expensive than chromating.

Electrically, the anodic films are also insulators. This property is used as a quality control detection of the anodic film. Such films are not usable in electromagnetic bonding, which is an increasingly stringent requirement of aerospace contracts.

The totals of positives and negatives favor choice of chromating over anodizing.

Plated Metals on Aluminum

In order to achieve the maximum in electromagnetic bonding, aluminum has been metal plated. The process of plating aluminum consists of first, cleaning and deoxidizing. The next step is the one which makes the aluminum plateable. Until this technique was developed, because of the dense oxide film formed in air or water, adherent metals could not be plated on aluminum. This critical operation consists of immersing the aluminum in a strongly alkaline solution containing zinc ions. Since aluminum is soluble in alkali, the oxide film is released. Then the galvanic potential developed in this medium causes the zinc to deposit on the aluminum. The zinc-coated aluminum may be plated with whatever metals are design required. Normally, copper is the first layer.

However, the commonly used plated metals, copper, tin and nickel, are, in the presence of atmospheric moisture, cathodic to the aluminum. Consequently, at a scratch in the plated metal,

galvanic corrosion of the aluminum occurs. Since corrosion products are oxides, non-conductors, degradation of electromagnetic bonding results.

A further limitation on use of plated metals on aluminum exists in that there is no method of restoration of damaged platings. If mechanical damage occurs, the only corrosion protection of the aluminum is by application of organic paints.

Touch up of plated metals by locallized plating ("brush plating") is a technique commonly used on heavy metals. This technique consists of making the part with the damaged area cathodic. The anode is encased in an absorbent material, to which is fed the plating electrolyte. Stroking of the encased anode over the cathode, electrodeposits the metal.

Unfortunately, the galvanic potential between the plated metals and the aluminum make it difficult to deposit an adherent metal layer at the interface. While some processors claim success, our own experience creates doubt about this interface. Apparently successful plating may, in this area, be only bridging.

Magnesium

Magnesium finishes fall into the same classes as those for aluminum, i.e., chromates, anodic films and platings. The processes are parallel. However, since magnesium is soluble in acids whereas aluminum is soluble in alkali, the composition and pH of the processing solutions are appropriately adjusted. Furthermore, since the magnesium is more susceptible to atmospheric oxidation and the galvanic potential between magnesium and the plated metals is greater, the protective value of the coatings is less than in the case of aluminum. This is true, especially in the case of castings, which are used as a manufacturing cost savings to avoid machining of boxes. The inherent porosity of the cast structure creates defects in the coatings, particularly platings. Residual contaminants from the casting process and entrapped electrolytes from the coating processes inhibit plating and cause corrosion at these sites. It is possible that corrosion problems and their repair may financially outweigh the financial benefits achieved by the casting technique.

Copper Alloys

In applications requiring high electrical conductivity, as for example connector contacts, copper, pure or alloyed, depending upon strength requirement, is used. Since, in ordinary atmospheres, copper tarnishes, consequently losing surface conductivity, hence it is plated with a non-tarnishing metal.

Copper Alloy Finishes

Gold is the most widely used protective finish for connectors (pure copper, in the case of circuit board contacts; and beryllium copper, in the case of their female counterparts). It has also been the strongest factor in corrosion of the copper. At any discontinuity in the gold, whether from a void occurring during the plating process or subsequent mechanical damage, the galvanic potential developed between the gold and the copper is such that salt bridges of corrosion deposits between contacts and actual severance of the contact fingers has resulted.

Chromates, similar in function to, although appropriately adjusted in function from those used on aluminum and magnesium, have proven capable of repairing voids in the gold plated surfaces. By process adjustment, the electrical resistance of these films has been maintained below the 2.5 milli-ohm per bond juncture requirements of MIL-B-5087.

Elimination of the gold would be desirable to avoid both expense and corrosion. Alternate metals considered are tin, which is feared because of possible "whisker" formation (ion migration under electrical potential), solder (60-40 tin-lead), and tin-nickel (60-40). The chromate film alone would ideally fit the cost and corrosion requirements. However, the films thus far developed are only marginally solderable using non-corrosive soldering flux (water white rosin (abietic acid)).

Cobalt-Nickel Iron

These alloys are used for the contacts which pass from the semiconductors through glass and are chosen for thermal coefficient match with the glass. Normally, plating of these leads occurs after their fusion into the glass. Therefore, inevitably, some area of metal adjacent to the glass is unplated and hence protected. This problem is independent of the nature of the plated metal, which must be a solderable one. Its seriousness is a function of the operating environment of the assembly.

Nickel-Iron Alloys and Iron-Silicon Alloys

These materials, which are used in magnetic and electrical applications, need corrosion inhibition primarily during storage and fabrication, the silicon iron being more corrosion susceptible than the nickel-iron. In operation, it is probable that each will be protected from the environment, e.g., by laminating with an organic polymer.

In-process protection of these materials can be accomplished with preservative oils, amines, chromates or phosphates.

Stainless Steels

Stainless steels are the most widely used materials for aerospace threaded fasteners. In general, their corrosion resistance decreases as their strength increases. For example, a passivated 18 Cr - 8 Ni alloy remains uncorroded, where, in the same environment, a precipitation hardening alloy shows some rust, and a 400 series material, e.g., 440C, will show more rust. While the 18-8 alloy is adequately protected by passivation, it may become necessary to plate or otherwise protect the 440C.

Passivation of stainless steels is accomplished, after chemical cleaning of the surfaces, by soaking in an oxidizing acid such as nitric or a mixture of nitric with hexavalent chromium. As stated earlier, the 18-8 or austenitic steels are not a corrosion problem. However, as the compositions are modified to produce strength by heat treatment, the corrosion resistance produced by passivation decreases.

Studies, Reference b, found that a maximum corrosion resistance for 440C (high strength, chromium iron alloy) may be achieved only if the surface to be passivated is free of heat oxide as evidenced by discoloration. Previously, a generalization had been heard that such discoloration was beneficial. The implications of this statement are serious. Expensive equipment and materials are required to maintain freedom from this oxidation/discoloration. Since most items are passivated in the finished machined condition, chemical etching to remove oxide is intolerable.

High Strength Steels

These materials are extremely susceptible to hydrogen embrittlement by chemical processing. The soaking in hydrochloric or sulfuric acid to deoxidize, which is the normal treatment to obtain adhesion is forbidden for these steels. Instead, only anodic treatment in sulfuric acid or a few seconds soak in 1/2% nitric acid is allowed. These extremely stringent requirements result from research whose results have been incorporated into military documents mandates, which require post-plating baking at 375 F for periods of three or 23 hours, depending on the strength level of the steel.

To exemplify the problems incurred by plating such materials, a small diameter wire spring was designed of cadmium plated music wire. The spring wire was coated with tin as a forming lubricant. After forming, it was heat treated without removal of the tin. (The spring manufacturer was not schooled in chemical processes or hydrogen embrittlement.) The oxidized tin could not be plated. The only scale removal technique which would not cause hydrogen embrittlement was abrasive blasting. The spring was so fragile that accidentally dropping to the ground would distort it beyond usability. In short, the design was literally not produceable in music wire. The music wire had been chosen because it could be made so high in tensile strength. What the designer had not known was that, in such small diameter, an 18 chromium - 8 nickel alloy could be cold worked to the required strength. Since it is inherently corrosion resistant, no plating would be required. Substitution of this alloy would have avoided the impossible-to-solve plating problems.

Summary

The foregoing examples provide ample evidence that protective systems should be carefully chosen during the early phases of product design. Such actions will assure that electronic structures will function more reliably during the required operating life.

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